

Preparation and Properties of Conjugated Polymers Containing 1,2-Diaryl-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene Units

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Conjugated polymers containing sterically protected 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene units were prepared and their properties were investigated. Red shifts of the polymers were observed, compared to the corresponding monomeric species, which indicates extension of the π system on polymerization.

Heteroatom-containing conjugated polymers are of current interest, because of their various functionalities.¹ Conjugated polymers containing π -bonded heavier main group elements are also attractive. Some polymers containing multiply bonded phosphorus atoms² have recently been prepared and their properties were investigated: Gates³ and Protasiewicz⁴ prepared π -conjugated polymers containing P=C bond in the main chain. However the polymers are either sensitive to oxygen or moisture,³ and the extension of the conjugation is supposed to be limited,⁴ because the P=C π -plane and the aromatic π -plane of the sterically protecting group are nearly perpendicular in energetically favored conformation.⁵ Thus, properties of other types of conjugated system containing multiply bonded phosphorus atoms are of interest.

We have reported preparation of the first polymer containing 3,4-diphosphinidenecyclobutene (abbreviated to DPCB) moieties and its polymer complex,^{6,7} as well as catalytic activity of the related DPCB-polymer.⁸ However the DPCB units are electronically isolated each other by methylene chains. We now report here preparations and properties of π -conjugated polymers containing the DPCB units. In these polymers, the phosphorus-carbon π -bonds are incorporated in the π -system of the polymer.

The synthetic route for the polymer is shown in Scheme 1. The DPCB derivatives are normally prepared from ethynylphosphines via bis(phosphaallene) intermediates.^{8,9} Thus, we prepared compounds **5a** and **5b**, as monomeric precursors. Compound **1a**,¹⁰ bearing an octyl group to increase polymer solubility, was prepared as follows. A Kumada coupling of 1,4-dibromobenzene with 3-octyl-2-thienylmagnesium bromide in the presence of Pd₂(dba)₃ and *N*-heterocyclic carbene ligand [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene chloride]¹¹ afforded **1a** in 89% yield,¹² while **1b**¹³ was prepared by the Suzuki coupling of 2,7-diiodo-9,9-dioctylfluorene and 2-thiopheneboronic acid in 91% yield. Reaction of **1a** and **1b** with NIS, followed by the Sonogashira coupling and desilylation, afforded **4a** and **4b** in 63 and 77% yield, respectively (in 3 steps). Compounds **4a** and **4b** were then converted to **5a** (87%) and **5b** (70%) by metallation of **4a** and **4b** with ethylmagnesium bromide in THF followed by reaction with chloro(2,4,6-tri-*t*-butylphenyl)phosphine.¹⁴ Compounds **5c** and **5d** (Chart 1) were also prepared from **4c** and **4d**¹⁵ in a similar manner (**5c**: 40% yield; **5d**: 48% yield).

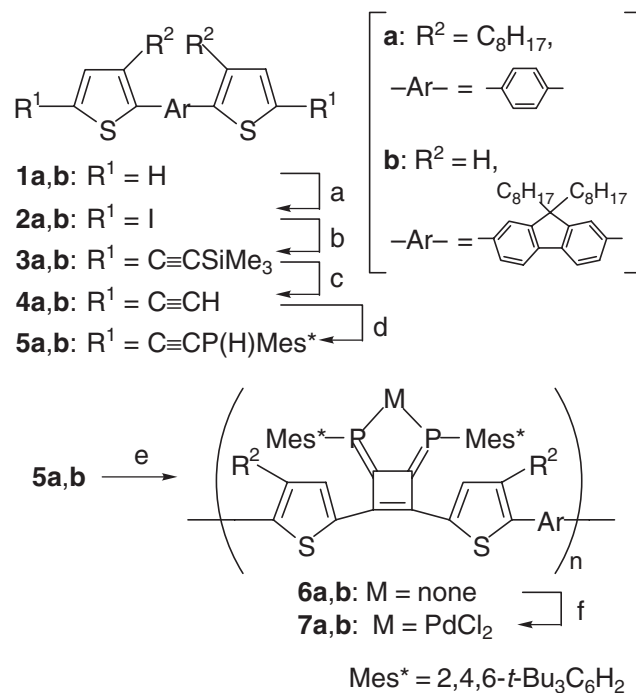
As the precursors **5a–5d** were obtained, preparation of the

polymers by a similar method reported previously⁸ were studied. Polymers **6a** and **6b** were successfully obtained from **5a** and **5b** in 32 and 38% yield, respectively, after reprecipitation from Et₂O-MeOH. These polymers turned out to be stable in air. The yields for **6a** and **6b** were better than that for alkylene-linked DPCB polymer **8**.⁸ On the other hand, attempted preparation of polymers from **5c** and **5d** resulted in the formation of complex mixtures of products including oligomeric products ($M_n < 3000$), probably because propagation was prevented by steric repulsion between the DPCB units.

6a: Red solid; ³¹P NMR (162 MHz, CDCl₃) δ 198.6 [br, (*E,Z*)-DPCB moiety], 177.1 [br, (*E,Z*)-DPCB moiety], 171.3 [br, (*E,E*)-DPCB moiety], and -71.8 (s, terminal moiety); IR (KBr) 1591, 1460 (br), 1392, 1362, 1238, 1203 (br), 1120, and 833 cm⁻¹; M_n 59600, M_w/M_n 72.4.¹⁶

6b: Red resin; ³¹P NMR (CDCl₃) δ 171.1 [br, (*E,E*)-DPCB moiety] and -71.6 (s, terminal moiety); IR (KBr) 1593 (br), 1460 (br), and 800 cm⁻¹; M_n 4500, M_w/M_n 4.4.

It should be mentioned that several problems for the alkylene-linked DPCB polymer **8** have been overcome in the case of **6**: (i) The solubility of **6** for common organic solvents was improved; (ii) in the preparation of **6**, intramolecular cyclization



Scheme 1. (a) NIS, CHCl₃, AcOH; (b) Me₃SiC≡CH, NEt₃, CuI, Pd(OAc)₂, PPh₃, DMF; (c) NaOH-MeOH, THF; (d) (i) EtMgBr, THF; (ii) Mes*P(H)Cl; (e) (i) *n*-BuLi, DME; (ii) BrCH₂CH₂Br, then reflux in toluene; (f) PdCl₂(MeCN)₂, THF.

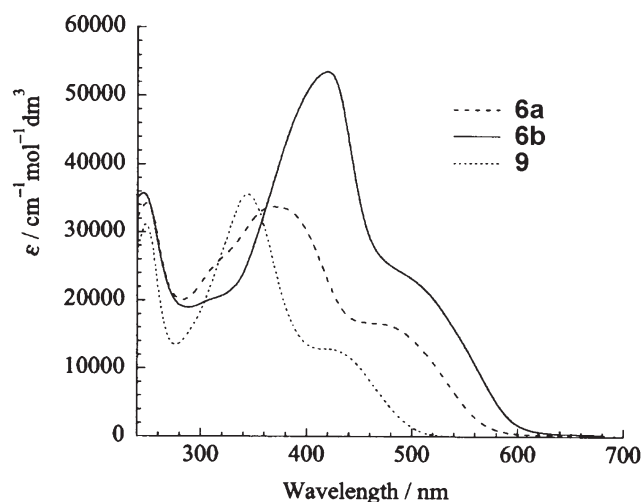


Figure 1. UV-vis spectra of **6a**, **6b** and **9** in CH_2Cl_2 . Molar absorption coefficients for **6a** and **6b** are calculated based on the formal repeating unit.

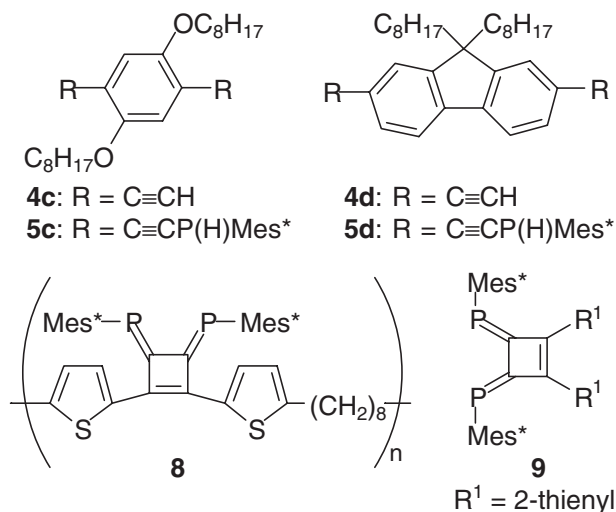


Chart 1.

was suppressed to lead to better yield due to the rigidity of linkers; (iii) polymer **6** is expected to show better electronic interaction between the DPCB moieties, due to π -conjugation: Figure 1 shows UV-vis spectra of **6a** and **6b** and the related compound **9**.^{9c} Apparent red shifts were observed in the π - π^* absorption bands of **6a** and **6b**, compared with that of **9**.¹⁷ These facts indicate relatively good π conjugation in **6a** and **6b**. The degree of the red shift is **6a** < **6b**, probably because the octyl group on the thienyl ring of **6a** hinders coplanarity between the thienyl and phenylene moieties.

Next, transition metal complex formation of the polymers was investigated. When 1 molar amount of $\text{PdCl}_2(\text{MeCN})_2$ was allowed to react with the polymers in THF at room temperature for 3 h, dark brown polymer complexes **7a** and **7b** were obtained in ca. 65% and 70% yield, respectively. **7a**: ^{31}P NMR (THF- C_6D_6) δ 152 (br.); IR (KBr) 1718, 1591, 1462, 1437, and 1122 cm^{-1} ; **7b**: ^{31}P NMR (THF- C_6D_6) δ 150 (br.); IR (KBr) 1724, 1595, 1460, 1265, 1122, 1072, and 802 cm^{-1} .¹⁸

This is the first example of the complex formation of conju-

gated polymer containing double bonded phosphorus. These polymer metal complexes can be regarded as an example of 'assembled complexes,' which are of current interest.¹⁹

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